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CHAIN BREAKING AND BRANCHING IN THE ACTIVE-PARTICLE DIFFUSION CONCEPT OF QUENCHING

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SUMMARY

General quenching-distance equations were derived as extensions of the original simple theory of quenching by diffusion of active particles. These equations take into account the possibility of gas-phase chain breaking and branching and the effect of the efficiency of the walls to destroy active particles. The general characteristics of the equations were examined.

All available types of propane quenching data from the literature were treated in a consistent manner. The data covered a thirtyfold range of quenching distances and included the effects of temperature, pressure, and propane and oxygen concentrations. Lean-to-stoichiometric mixtures were treated.

The effects of elevated initial temperature were predicted by means of the simple theory, and were found to agree qualitatively with the observed trends.

The simple theory correlated all the available propane quenching data satisfactorily. From this agreement, it was concluded that gas-phase chain breaking and branching may be neglected in the treatment of quenching data for propane-oxygen-nitrogen flames. It was also concluded that the walls may be considered 100 percent efficient for the destruction of active particles.

These conclusions are meaningful only in connection with the general concepts of flame quenching by diffusion of active particles, and do not establish the validity of the concepts.

INTRODUCTION

The quenching action of the walls on a flame is an important phenomenon in combustion. Consideration must be given to quenching in most

(3) Chain-branching reaction (The reaction of one active particle produces more than one new active particle.)

(4) Chain-breaking reaction (The active particle is destroyed.)

Active particles diffuse to the walls of the quenching channel as well as into the unburned gas. It was assumed that a fraction ε of the active particles that strike the walls are destroyed. The shape of the quenching channel has an effect on the amount of diffusion to the walls; it was assumed that the equations applicable to the case of a channel formed by infinite plane-parallel plates were approximately correct for long rectangular slots. Reference 8 investigated the end effects of rectangular slots and found that they were small in most cases.

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Straight- and branched-chain reactions promote flame propagation, while chain breaking in the gas phase and at the wall tends to quench the flame. Thus, the flame will be quenched if the chain-breaking reactions predominate.

Derivation of Equations

Reference 6 sets up the following simple criterion for a flame to propagate through a volume element in a quenching channel:

$$\sum_i \nu_i N_i = A N_t \tag{1}$$

Equation (1) states that a flame cannot propagate unless the total number of effective collisions of active particles is equal to a critical fraction A of the total number of molecules present in the gas phase. This criterion has been retained in the present work. Introduction of the factors of chain breaking and branching in the gas phase and of incomplete destruction of active particles at the walls merely changes the expression for the chain length ν_i.

General equations; chain breaking and branching in gas phase; $\varepsilon \neq 1$. - In the derivation of the expression for the chain length, it is necessary to introduce chain-branching and -breaking coefficients f and g, respectively. These coefficients have dimensions of reciprocal seconds and express the average frequency with which active particles take part in branching and breaking reactions. There is one solution for the case $(f - g) > 0$ (branching predominates) and two solutions for the case $(g - f) > 0$ (breaking predominates). The differential equation for diffusion of active particles in a duct formed by infinite plane-parallel plates is as follows (see refs. 12 and 13, and appendix):

$$D_i \frac{d^2 c_i}{dx^2} + (f_i - g_i)c_i + c_{o,i} = 0 \tag{2}$$

subject to the boundary conditions

$$\left.\begin{aligned} c_i &= c_{w,i} \\ x &= \pm d/2 \end{aligned}\right\} \quad \text{and} \quad \left.\begin{aligned} \frac{dc_i}{dx} &= 0 \\ x &= 0 \end{aligned}\right\} \tag{3}$$

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The details of the derivation are given in the appendix. The following equations are obtained:

Chain branching:

$$d^2 = \frac{\left(\frac{\pi^4}{8}\right)\left[A - \frac{(1 - \varepsilon)\ 0.7}{kN_f + (f - g)} \sum_i \frac{p_i}{p}\right]\left(\frac{T_R}{T_O}\right)^n}{kN_f \left[1 + \frac{(1 - \varepsilon)\ 0.7}{1 + \frac{kN_f}{(f - g)}}\right] \sum_i \frac{p_i}{D_i^o} \left[\frac{1}{1 - \frac{pd^2(f - g)}{\pi^2 D_i^o}\left(\frac{T_O}{T_R}\right)^n}\right]} \tag{4}$$

where

$(f - g) > 0$, and $d/2\sqrt{(f - g)/D_i} < \pi/2$

Small amount of chain breaking:

$$d^2 = \frac{12\left[A - \frac{(1 - \varepsilon)\ 0.7}{1 - \frac{(g - f)}{kN_f}} \sum_i \frac{p_i}{p}\right]\left(\frac{T_R}{T_O}\right)^n}{kN_f \left[1 + \frac{(1 - \varepsilon)\ 0.7}{1 - \frac{kN_f}{g - f}}\right] \sum_i \frac{p_i}{D_i^o} \left[1 - \frac{pd^2(g - f)}{10\ D_i^o}\left(\frac{T_O}{T_R}\right)^n\right]} \tag{5}$$

d	width of rectangular slot, cm
d_c	diameter of cylinder, cm
f	average chain-branching coefficient, sec^{-1}
f_i	chain-branching coefficient for active particles of one kind, sec^{-1}
g	average chain-breaking coefficient, sec^{-1}
g_i	chain-breaking coefficient for active particles of one kind, sec^{-1}
k	average specific rate constant for reaction of H, O, and OH with fuel molecules, $cm^3/(molecule)(sec)$
m	power expressing variation of quenching distance with initial mixture temperature, $d \propto T_0^m$
N_f	number of fuel molecules per unit volume, $number/cm^3$
$N_f(T_R)$	number of fuel molecules per unit volume in unburned mixture at reaction temperature, $number/cm^3$
N_i	number of active particles of one kind per unit volume, $number/cm^3$
N_t	total number of molecules per unit volume, $number/cm^3$
n	power expressing temperature dependence of diffusion coefficient, $D \propto T^n$
p	total pressure of mixture, atm
p_H, p_O, p_{OH}	equilibrium adiabatic partial pressure of H, O, and OH, respectively, atm
p_i	partial pressure of active particles of one kind, atm
$p_i(eq)$	equilibrium adiabatic partial pressure of active particles of one kind, atm

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T_0 initial mixture temperature, $^\circ K$

T_R mean reaction temperature in preflame zone, $^\circ K$

$T_F(eq)$ equilibrium adiabatic flame temperature, $^\circ K$

x,y,z Cartesian coordinates

ε fraction of total number of active particles striking walls that are destroyed

ν_i chain length; that is, average number of effective collisions of an active particle of one kind with gas-phase molecules before the particle is destroyed

Ψ $$\left(\frac{12}{N_f}\right)\left(\frac{T_R}{T_0}\right)^n \left[\frac{1}{\left(\frac{p_H}{D_H^o} + \frac{p_O}{D_O^o} + \frac{p_{OH}}{D_{OH}^o}\right) 0.7}\right]$$

τ_i average time between effective collisions of an active particle of one kind with fuel molecules, sec

ACTIVE-PARTICLE DIFFUSION CONCEPT OF QUENCHING

Description of Model

The quenching equations were derived from a generalized form of the model of the quenching process described in reference 6. It was assumed that the light, rapidly diffusing active particles, H, O, and OH, are necessary for flame propagation in hydrocarbon-air mixtures. The rate-controlling step in the combustion chain reaction is presumed to be between these active particles and fuel molecules and to take place ahead of the zone of maximum temperature rise. The concentration of active particles in the preflame zone is maintained by diffusion. This is the model treated by Tanford and Pease in their theory of burning velocity (refs. 10 and 11).

Four types of collisions were considered between active particles and other particles in the gas phase:

(1) Collision without any essential effect upon the active particle

(2) Reaction with a fuel molecule and subsequent regeneration after a chain of more rapid reactions (A series of such steps constitutes a simple, straight-chain reaction.)

studies of other flame properties. For example, Coward and Jones have pointed out the need to measure concentration limits of flammability in tubes large enough to preclude quenching effects (ref. 1); Lewis and von Elbe have described the relation of quenching by the electrodes to spark-ignition energy (ref. 2).

For cylinders and plane-parallel plates, the quenching effect may be characterized experimentally in terms of the quenching distance, the smallest opening of a channel that will permit flame propagation. Quenching distance depends on the geometry of the channel and on the pressure, temperature, and composition of the combustible mixture.

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Quenching offers a field for theoretical interpretation that has not been very thoroughly explored. In contrast to other flame phenomena, it is not difficult to assign plausible boundary conditions to the flame in proximity to walls. For example, the walls might be considered to be an essentially infinite sink for both heat and active particles (atoms and free radicals), the wall temperature to be the ambient temperature, and the active-particle concentration to be zero at the walls.

References 2 and 3 describe a theory of quenching based on the loss of heat from the flame to the wall that utilizes the combustion-wave theory of Lewis and von Elbe. The results were applied to quenching-distance data in references 2 and 4. Mixtures of methane and propane with oxygen and nitrogen were considered. A less comprehensive analysis, also based on heat loss to the walls, was presented in reference 5 to interpret the effects of various inerts on the quenching distances of hydrogen-oxygen-inert mixtures.

More recently, equations have been derived that express the quenching distance in terms of a balance between the number of active particles lost by diffusion to the walls and the number that must diffuse into the fresh gas to sustain flame propagation (ref. 6). These equations have been tested with some success for a larger number of experimental situations than either of the thermal theories. The equations in their present form apply only to lean-to-stoichiometric mixtures. Reference 6 interpreted quenching distances for lean-to-stoichiometric propane-, ethene-, and isooctane-air mixtures at various reduced pressures; the geometrical factor to account for the difference between tubes and long rectangular slots was also predicted and reasonably well confirmed. Reference 7 extended the application of the equations to quenching distances obtained for propane-oxygen-nitrogen mixtures over a range of pressures. Reference 8 dealt quite successfully with the predicted and observed geometrical differences between cylinders, annuli, and rectangular slots of various length-to-width ratios, as compared with the idealized case of infinite plane-parallel plates.

The equations developed in reference 6 were based on the following simple model of the chemical processes of flame propagation: (1) The rate-determining reaction is between fuel molecules and the light, rapidly diffusing active particles H, O, and OH; (2) there is no chain breaking or branching in the gas phase; (3) every active particle that strikes the walls is destroyed.

The purpose of this report is to develop general equations for flame quenching, based on the active-particle diffusion model of reference 6. The previous restrictions are removed. Chain breaking and branching in the gas phase are considered, as well as incomplete destruction of active particles at the walls. The general equations are discussed in relation to all available types of quenching-distance data for lean-to-stoichiometric mixtures of propane with oxygen and nitrogen, including data that show the effects of initial mixture temperature (ref. 9). All the data considered are for long, rectangular quenching channels. The sensitivity of the results to the choice of diffusion coefficients and of the temperature dependence of the diffusion coefficients is also tested.

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SYMBOLS

The following symbols are used in this report:

A	fraction of total molecules present in the gas phase that must react if the flame is to continue to propagate
c_i	concentration of active particles of one kind at any point across channel, number/cm^3
$c_{o,i}$	rate of production of active particles of one kind, number/$(cm^3)(sec)$
$c_{w,i}$	concentration of active particles of one kind at the walls, number/cm^3
D_i	diffusion coefficient for active particles of one kind, cm^2/sec
D_i^o	diffusion coefficient for active particles of one kind into unburned gas at atmospheric pressure and initial mixture temperature, cm^2/sec
D_H^o, D_O^o, D_{OH}^o	diffusion coefficient for H, O, and OH, respectively, into unburned gas at atmospheric pressure and initial mixture temperature, cm^2/sec

where

$(g - f) > 0$, and $(g - f)\, d^2/D_i < 1$

Large amount of chain breaking:

$$d = \frac{\sum_i \left[\frac{kN_f}{g - f} - \frac{(1 - \varepsilon)\, 0.7}{1 - \frac{g - f}{kN_f}} \right] \frac{2p_i}{\sqrt{\frac{(g - f)\, p^3 \left(\frac{T_O}{T_R}\right)^n}{D_i^O}}}}{\sum_i \left(\frac{kN_f}{g - f} \right) \frac{p_i}{p} - A} \tag{6}$$

where

$(g - f) > 0$, and $(g - f)\, d^2/D_i > 2$

No chain branching or breaking in gas phase; $\varepsilon \neq 1$. - It was desired to derive the quenching equation for this less general case for direct comparison with the result derived in reference 6, in which gas-phase chain breaking and branching and incomplete destruction of active particles at the walls were not considered. The differential equation of diffusion is:

$$D_i \frac{d^2 c_i}{dx^2} + c_{o,i} = 0 \tag{7}$$

subject to the boundary conditions

$$\left.\begin{aligned} c_i &= c_{w,i} \\ x &= \pm d/2 \\ \text{and} \\ \frac{dc_i}{dx} &= 0 \\ x &= 0 \end{aligned}\right\} \tag{8}$$

The details of the solution are given in the appendix. The following equation is obtained:

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$$d^2 = \frac{12\left(\frac{T_R}{T_O}\right)^n \left[A - \frac{(1 - \varepsilon)\ 0.7}{p} \sum_i p_i(eq)\right]}{kN_f \sum_i \frac{p_i}{D_i^o}} \tag{9}$$

The solutions of equation (2) do not reduce to the solution of equation (7), when $f - g$ is set equal to zero, because they are solutions of a basically different differential equation.

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It is also shown in the appendix that the geometry effect to be expected in comparing quenching in cylindrical and rectangular channels is the same as that predicted in reference 6, subject to the assumption $\varepsilon = 1$.

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For the sake of brevity, following reference 7, equation (9) may be rewritten as

$$d^2 = \left(\frac{A}{k}\right) \psi \left[1 - \frac{(1 - \varepsilon)\ 0.7}{Ap} \sum_i p_i(eq)\right] \tag{10}$$

where

$$\psi = \left(\frac{12}{N_f}\right)\left(\frac{T_R}{T_O}\right)^n \left[\frac{1}{\left(\frac{p_H}{D_H^o} + \frac{p_O}{D_O^o} + \frac{p_{OH}}{D_{OH}^o}\right)0.7}\right] \tag{11}$$

APPLICATION OF QUENCHING EQUATIONS

General Equations

The general expressions for quenching distance (eqs. (4) to (6)) cannot be completely evaluated at present. The basic reason for this is that the mechanisms of active-particle reactions are not sufficiently understood. For example, the most general forms of the equations should allow for separate chain-branching and -breaking coefficients f_i and g_i for each species of active particle. Furthermore, f_i and g_i are expected to vary with temperature, pressure, and mixture composition (ref. 12, p. 36). In view of the lack of information on these subjects, the specific coefficients have been replaced by average coefficients f and g in equations (4) to (6); f and g are assumed to be the same for all active particles. A similar procedure was used in reference 6, where individual rate constants k_i for the reaction between active particles and fuel molecules were replaced by an average rate constant k.

There is a similar lack of information with respect to ε, the efficiency of the wall to destroy active particles. There have been many studies of the effects of wall materials on the low-temperature oxidation of hydrocarbons (ref. 2), but these results are probably not applicable to high-temperature oxidation in flames. Other studies specifically designed to measure the recombination of active particles on walls are also of doubtful value for the purposes of the quenching-distance equations. In such work, care is taken to provide a known, reproducible surface in each experiment; in flame-quenching experiments, on the other hand, a wall that has been exposed to hot combustion products cannot be expected to remain uncontaminated. This is probably the reason for the usual failure to observe any effect of different wall materials on quenching distance (ref. 9); however, experiments in flame tubes, which were carefully treated before the passage of each flame, did indicate that wall effects can be observed if the work is done properly (ref. 2, p. 335).

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In spite of the difficulties described, something may be gained by a discussion of the characteristics of the general quenching equations. Furthermore, rough quantitative estimates of the quantities $f - g$ and $g - f$ may be derived from the equations, with the aid of calculated flame temperatures and partial pressures of H, O, and OH. Such calculations have previously been reported (refs. 6 and 7) for the ranges of pressure, propane concentration, and oxygen concentration covered by the quenching-distance data of references 7 and 9. In order to include the data of reference 9 that show the effects of initial mixture temperature on quenching distance in the present discussion, some additional values of equilibrium adiabatic flame temperature and partial pressures of active particles were computed and are listed in table I. The calculations were carried out by the matrix method of reference 14, using the thermodynamic constants tabulated in reference 14 and the heat of formation of propane in reference 15.

Inasmuch as the model contemplates a flame approaching the quenching channel and considers the events in some mean plane of reaction ahead of the flame front, it is necessary to choose values for the terms N_f, T_R, and p_i. The choice made in reference 6 was to express the terms as functions of the equilibrium adiabatic flame temperature and active-particle concentrations, since these quantities can be calculated. The following relations were chosen in reference 6, and are used herein:

$$T_R = 0.7\ T_F(eq) \tag{12}$$

$$p_i = 0.7\ p_i(eq) \tag{13}$$

$$N_f = 0.5\ N_f(T_R) \tag{14}$$

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Chain branching; equation (4). - A chain-branching reaction occurs if, on the average, each active particle that disappears in one of the steps of the chain mechanism gives rise to more than one new active particle. Thus, there is the possibility of a run-away reaction; in the limit, the chain length may become infinite, and cause a homogeneous explosion. In such a case, the reaction cannot be quenched by the walls.

The solution embodied in equation (4) is subject to the following restriction on the chain-branching parameter:

$$\frac{d}{2}\sqrt{\frac{f - g}{D_i}} < \frac{\pi}{2} \tag{15}$$

Further, this is not merely a limit to the range of values for which the approximate expression for the chain length holds; it is also a physical limit. For the condition

$$\frac{d}{2}\sqrt{\frac{f - g}{D_i}} = \frac{\pi}{2} \tag{16}$$

the chain length becomes infinite (see appendix). Since flames, not homogeneous explosions are of concern, and since the flames are at the quenching condition, the chain length clearly cannot be infinite. However, equation (16) may be used to estimate the upper limit for $f - g$. If D_i is expressed in terms of the diffusion coefficient at 1 atmosphere and initial temperature,

$$D_i = D_i^o \left(\frac{1}{p}\right)\left(\frac{T_R}{T_O}\right)^n \tag{17}$$

Substituting equation (17) into equation (16) yields

$$\frac{pd^2(f - g)}{\pi^2 D_i^o}\left(\frac{T_O}{T_R}\right)^n = 1 \tag{18}$$

Comparison of equation (18) with the second bracketed term in the denominator of equation (4) shows that the equation is consistent with the fact that homogeneous explosions are not quenched by walls, inasmuch as the condition for infinite chain length is also the condition for zero quenching distance.

A mixture will certainly explode if the frequency of branching is the same as the frequency of reaction; that is, if every reaction of an active particle produces more than one new particle. Now, the average

rate constant for the reaction of active particles with fuel k seems to be $\sim 10^{-13}$ cubic centimeter per molecule per second (ref. 17); the frequency of effective collisions between active particles and fuel molecules kN_f is therefore 10^3 to 10^4 per second. If a single value of $f - g$ is required to satisfy the criterion of equation (18) for all the experimental points, it should consequently be of the same order of magnitude as kN_f in the limit of infinite chain length. Inspection of the quenching-distance data of references 7 and 9 and of the calculated values of T_R shows that $f - g$ may indeed be of the order of 10^3 per second at the limit expressed by equation (18). The limit of the equation is therefore consistent with the statement that a mixture will explode if the frequency of branching is the same as the frequency of reaction.

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It has already been stated that the coefficients f and g are expected to vary with temperature, pressure, and composition of the mixture, but that little or nothing is known about these variations in the case of hydrocarbon flame reactions. The quenching equation (eq. (4)) can add nothing to the knowledge of the branching reaction itself. However, the term $f - g$, expressing an over-all chain-branching reaction, may be briefly discussed. If $f - g$ is considered constant (despite the expected variations), the variables with which $f - g$ is associated in equation (4) show that a constant amount of over-all chain branching would be a more important factor in the less vigorous mixtures in which large quenching distances are associated with relatively high pressures and low reaction temperatures.

Chain breaking; equation (5). - If a sufficient amount of chain breaking takes place in the gas phase, no chemical reaction occurs in the limit; a flame cannot burn, no matter how far the walls are separated.

Equation (5) is one of the two solutions for the case of over-all chain breaking in the gas phase and is valid for small values of the chain-breaking parameter $g - f$. The restriction applicable to this solution is

$$\frac{(g - f)d^2}{D_i} < 1 \tag{19}$$

or, with D_i written in terms of D_i^o by means of equation (17),

$$\frac{pd^2(g - f)}{D_i^o}\left(\frac{T_O}{T_R}\right)^n < 1 \tag{20}$$

Equation (20) is not a physical limit; it is only a limit to the range of values of the chain-breaking parameter for which an expression for the chain length is a good approximation (see appendix). If $g - f$ is required to be a constant for all the propane quenching data, its value is limited by equation (20) to about 10^2 per second. This is, at most, only 10 percent of kN_f and is probably a negligible amount of chain breaking.

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It is seen from equation (5) that the quenching distance becomes infinite under the following conditions:

$$\frac{pd^2(g - f)}{10\, D_i^o} \left(\frac{T_o}{T_R}\right)^n = 1 \tag{21}$$

Thus, when this condition is satisfied, gas-phase chain breaking is capable of quenching the flame no matter how remote the walls may be, and equation (5) is consistent with the general statement made at the beginning of this section. Equation (21) is almost identical to equation (18), which is the condition for zero quenching distance in the chain-branching case. As before, the equation gives no information about the chain-breaking reaction itself; but, if a constant value of $g - f$ is assumed, it will be a relatively more important factor in weakly burning mixtures.

Chain breaking; equation (6). - The larger the fraction of molecules that must react to sustain flame propagation, the smaller the amount of chain breaking that can be tolerated by the flame. Equation (6), which is applicable to larger values of the chain-breaking parameter $g - f$, can be shown to take a form consistent with this statement.

It will be shown in a later section that the assumption $\varepsilon = 1$ is probably a good one. If equation (6) is rewritten subject to this assumption, the following form is obtained:

$$d = \frac{\dfrac{kN_f}{g - f} \displaystyle\sum_i \frac{2p_i}{\sqrt{\dfrac{(g - f)\, p^3 \left(\dfrac{T_o}{T_R}\right)^n}{D_i^o}}}}{\displaystyle\sum_i \left(\frac{kN_f}{g - f}\right) \frac{p_i}{p} - A} \tag{22}$$

Here, it is assumed as before that $g - f$ is a constant.

Equation (22) shows that the quenching distance becomes infinite, that is, gas-phase chain breaking becomes overwhelming, if

$$\frac{kN_f}{g - f}\sum_i \frac{p_i}{p} = A \tag{23}$$

Since $kN_f \sim 10^3$ to 10^4 and $\sum_i p_i/p \sim 10^{-3}$, then, very approximately,

$$(g - f) \sim 1/A \tag{24}$$

Thus, equation (6) leads to the expected relation between A and $g - f$.

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Treatment of Experimental Data

All available types of quenching-distance data should be correlated by a suitable form of the equations, if the diffusion concept of quenching is to be of value. The literature contains data that show the effects of pressure, fuel concentration, and proportion of oxygen in the oxidant atmosphere for propane-oxygen-nitrogen mixtures (ref. 7) and the effects of pressure, fuel concentration, and initial temperature, for propane-air mixtures (ref. 9). It should again be emphasized that the equations do not hold for rich mixtures in their present form; all the data to be treated in this report are therefore limited to lean-to-stoichiometric mixtures.

It has already been pointed out that the general equations (eqs. (4) to (6)) contain the chain-branching and -breaking parameters f and g about which very little is known. Therefore, it is impossible to evaluate these equations numerically at present. It is, however, both possible and instructive to evaluate equation (10), for the case of incomplete destruction of active particles at the walls, and the following equation, derived in reference 6 on the assumption that every particle striking the walls is destroyed:

$$d^2 = \left(\frac{A}{k}\right)\psi \tag{25}$$

The function ψ is defined by equation (11). Equation (25) has been applied to propane quenching data previously (refs. 6 to 8); but a consistent treatment has not been used for all the available types of data.

Numerical evaluation of any of the forms of the equations involves a choice of the diffusion coefficients for the active particles into the unburned gas at T_0, and a choice of the temperature dependence of the

diffusion coefficients. This temperature dependence is expressed by the exponent n. Two different sets of values have been used in previous applications: (1) Reference 6 employed the diffusion coefficients calculated in reference 16, with a temperature dependence $D \propto T^2$; (2) reference 7 gave more sophisticated values of the coefficients, accounted for the small effects of propane concentration, and assigned a temperature dependence $D \propto T^{1.67}$. It was decided in the present work to make separate comparisons of all the types of data for the two sets of diffusion coefficients in order to determine whether the data were fitted better by one set of values than by the other. Table II summarizes the two sets of diffusion coefficients and the assigned temperature dependencies.

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The values of ψ calculated subject to a temperature dependence of the diffusion coefficients $D \propto T^2$ will be designated ψ_1; those calculated subject to $D \propto T^{1.67}$ will be designated ψ_2.

Limiting values of ε; $\varepsilon \neq 1$ (eq. (10)). - In order to apply equation (10) to the experimental data, it was written in the following form:

$$d^2 = \left(\frac{A}{k}\right) \psi \left[1 - K \sum_i \frac{p_i(eq)}{p}\right] \tag{26}$$

where

$$K = \frac{(1 - \varepsilon)\ 0.7}{A} \tag{27}$$

and

$$\sum_i \frac{p_i(eq)}{p} = \left(\frac{1}{p}\right)(p_H + p_O + p_{OH}) \tag{28}$$

The factor 0.7 (eq. (27)) expresses the average concentration of active particles in a volume element across the quenching channel ahead of the flame front and is introduced by equation (13).

Several arbitrary values of the destruction-efficiency parameter K were chosen, and the quantity $\psi \left(1 - K \sum_i p_i(eq)/p\right)$ was calculated for both ψ_1 and ψ_2. The bracketed term became negative in some cases if K was greater than about 10. Larger values of K were therefore ruled out on physical grounds, since they would lead to imaginary quenching distances.

This upper limit on K permits an estimate of the permissible range of ε. From equation (27),

$$\varepsilon = 1 - \frac{10\,A}{0.7} \tag{29}$$

The fraction of molecules A that must react for the flame to propagate refers to a plane ahead of the zone of maximum temperature rise on the fresh-gas side of the flame. It is therefore evident that A cannot be larger than the mole fraction of fuel at the lean limit of flammability. If A is taken as the lean limit, 0.0201 (ref. 17), equation (29) yields $\varepsilon \sim 0.7$. If, on the other hand, A is less than the lean limit, ε increases. Inasmuch as the upper limit is, by definition, $\varepsilon = 1$, the estimated range is $0.7 \leq \varepsilon \leq 1$. It should be noted that this result can only be considered approximate, because it depends upon the choice of the factor 0.7 to express the average concentration of active particles.

Equation (26) does not correlate the quenching-distance data very well. A typical example is shown in figure 1, a logarithmic plot of d^2 against $\psi_2\left(1 - K\sum_i p_i(eq)/p\right)$ for $K = 10$; it is assumed, as in references 6 to 8, that the ratio A/k is constant. It will be noted that there is a great deal of scatter in this correlation.

Evaluation of simple quenching equations; $\varepsilon=1$ (eq. (25)). - Equation (25) is the quenching-distance equation developed in reference 6, without consideration of chain breaking or branching in the gas phase, and with the assumption that every active particle striking the walls is destroyed. As stated previously, equation (25) has been used to treat several types of quenching data (refs. 6 to 8), but the data of reference 9 that show the effects of initial mixture temperature have not previously been analyzed. Therefore, the agreement between the observed variation of quenching distance with initial temperature and the variation predicted by equation (25) is briefly described before proceeding to a general treatment of all the types of data.

Values of ψ (eq. (11)) were calculated for initial mixture temperatures of 0°, 300°, 400°, 600°, and 700° K and a pressure of 0.9731 atmosphere. The data of reference 9 were obtained for propane-air mixtures at the same pressure, but for a more limited range of temperatures (300° to 558° K). The calculation of ψ for an initial mixture temperature of 0° K was carried out with 300° K as the base temperature for the diffusion coefficients in order to avoid making the denominator of equation (11) equal to zero.

Figure 2 shows plots of the observed quenching distance, $\psi_1^{1/2}$, and and $\psi_2^{1/2}$ against initial temperature for four lean-to-stoichiometric

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propane-air mixtures. If, in equation (25), the ratio A/k is considered to be independent of initial temperature, the plots of $\psi_1^{1/2}$ and $\psi_2^{1/2}$ against T_0 show the predicted trend of quenching distance with initial temperature. Figure 2 indicates that equation (25) gives qualitative agreement with experiment in regard to the order and relative spacing of the curves for 3.00, 3.25, 3.50, and 4.03 (stoichiometric) percent by volume propane in air, regardless of the assumptions made for the diffusion coefficient. Furthermore, the almost linear dependence of quenching distance on initial temperature observed over the relatively short range of conditions studied in reference 9 is predicted by the variation of ψ_1 and ψ_2 over the same range.

The variation of quenching distance with temperature may be expressed by the exponent m on the assumption that $d \propto T_0^{-m}$. As reported in reference 9, m is about 0.5 for stoichiometric mixtures and increases for leaner mixtures. Values of m calculated by the method of least squares from the data of reference 9 are listed in table III; the values range from 0.60 for 4.03 percent by volume (stoichiometric) mixtures to 0.90 for 3.00 percent mixtures. The predicted temperature variations may be obtained from the analogous assumptions, $\psi_1^{1/2} \propto T_0^{-m_1}$ and $\psi_2^{1/2} \propto T_0^{-m_2}$. Values of m_1 and m_2 are also given in table III, and it is seen that the variations predicted from both ψ_1 and ψ_2 are qualitatively correct with regard to the dependence on propane concentration. However, the variation of $\psi_1^{1/2}$ with T_0 is less and that of $\psi_2^{1/2}$ is more than is shown by the observed quenching distances. It should be noted that these observations concerning figure 1 are governed by the assumption that the ratio A/k is independent of initial temperature; the results obtained when a reasonable temperature dependence is assigned are further discussed in a subsequent section. It may be concluded for the present that the simple diffusion concept of quenching gives fair predictions of the effects of initial temperature.

Figure 3 correlates all the available types of quenching-distance data by means of equation (25). Included are the effects of initial temperature, pressure, propane concentration, and proportion of oxygen in the oxygen-nitrogen oxidant atmosphere (refs. 7 and 9). Other experiments that show only the effects of geometry (refs. 6 and 8) have been omitted. As stated previously, only lean-to-stoichiometric mixtures are considered. Logarithmic plots are used in order to expand the scale; on straight plots, many of the points would be near the origin.

The left-hand portions of figures 3(a) and (b) show plots of d^2 against ψ_1 and ψ_2, respectively. Straight lines with a slope of unity

are drawn through the points, on the assumption that the ratio A/k is a constant for all the data. It is seen that both ψ_1 and ψ_2 give good correlations; the included range of conditions causes about a thirty-fold variation in the quenching distance.

However, the points for elevated initial temperatures deviate consistently in figure 3(a) from the line defined by the rest of the points. In figure 3(b), the corresponding points lie closer to the line. It therefore appears that increase of the initial mixture temperature above 300° K introduces effects that are reasonably well accounted for by values of ψ based on the diffusion coefficients of reference 7 with a temperature dependence $D \propto T^{1.67}$. However, close comparison of figures 3(a) and (b) shows that the points other than those for elevated temperatures are slightly better distributed about the line for d^2 against ψ_1. In addition, the possible dependence of A and k on initial temperature should be considered.

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Increase of the initial mixture temperature from 300° to 600° K, the approximate range of the data of reference 9, causes a maximum increase in the calculated mean reaction temperature T_R of 200° K. Inasmuch as the data remaining correlate so well in figure 3, even though they represent a range of T_R from 1350° to 2000° K, the average rate constant is apparently insensitive to temperature variation for the purposes of correlation.

The constant A, defined as the fraction of molecules present in the gas phase that must react if the flame is to propagate, may on the other hand depend on the initial temperature. Reference 6 showed that quenching distances could be calculated from equation (25) with an average deviation of only 3 percent when A was taken as the mole fraction of fuel at the lean flammability limit, and k was taken as the semiempirical rate constant derived from burning velocity measurements (ref. 16). If A is actually the mole fraction at the lean limit, there definitely should be a dependence on initial temperature; it is well known that the lean-limit concentration decreases nearly linearly with increased temperature (ref. 1). Wohl has objected to such an interpretation of A (ref. 18); nevertheless, A may be expected to vary with temperature in the same manner as the lean limit, even though it may not be correct to set it equal to the lean limit. This conclusion is drawn from the behavior of lean-limit flames: the increased enthalpy of a combustible mixture due to a higher initial temperature is just offset by an equivalent decrease in the heat of combustion of the limit mixture, so that a certain minimum enthalpy per unit area appears to be necessary for a flame to propagate (refs. 1 and 19). It is reasonable that similar considerations should also apply to other than limit flames.

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The factor A (eq. (25)) was therefore set equal to the mole fraction of fuel at the lean flammability limit. The value of A was taken as 0.0201 for all propane-oxygen-nitrogen mixtures at 300° K (ref. 17). No data were found in the literature on the variation of the lean limit of propane with initial temperature. It was therefore assumed that the percentage change in lean-limit equivalence ratio of propane with temperature is the same as that determined for n-pentane (ref. 1). This assumption leads to a predicted decrease of 0.19 percent by volume in the lean-limit concentration per 100° C temperature increase. The result is corroborated by a limited amount of unpublished NACA data, which give the variation as 0.20 percent by volume per 100° C temperature increase.

Plots of d^2 against $A\psi_1$ and $A\psi_2$ are shown in the right-hand portions of figures 3(a) and (b), respectively. It is again emphasized that variation of A with initial temperature is the important feature, not the absolute magnitude of A. The figures show that the elevated-temperature data are correlated considerably better by $A\psi_1$ than by ψ_1; the opposite is true for ψ_2 and $A\psi_2$, because ψ_2 alone correlates these data quite well.

DISCUSSION

Figure 3 shows that the simple diffusion theory of quenching correlates a wide range of quenching-distance data quite well. Variations in pressure, temperature, propane concentration, and oxidant atmosphere are included. Similar results are obtained with either of the two sets of diffusion coefficients. However, the logical assignment of a temperature variation for A somewhat favors a temperature dependence of the diffusion coefficients of the form $D \propto T^2$ rather than $D \propto T^{1.67}$ for purposes of the theory.

It is suggested that quenching distances for propane-oxygen-nitrogen mixtures may be reasonably well calculated by means of equation (25) if A is taken as the lean flammability limit and k is taken as the value derived from the right-hand line of figure 3(a), namely, 2.25×10^{-13} cubic centimeter per molecule per second. The value of A should be the appropriate one for the initial mixture conditions.

The general quenching-distance equations developed in this report cannot be evaluated numerically, because of insufficient knowledge about the chain-branching and -breaking parameters f and g. However, as previously pointed out, the equations show that, for constant values of f - g or g - f, these factors will be more important in the less vigorous mixtures. Reference 7 includes data for both weak mixtures

$(O_2/(O_2 + N_2) = 0.17)$ and vigorous mixtures $(O_2/(O_2 + N_2) = 0.70)$; inasmuch as figure 3 does not show any consistent deviations of these data from the simple theory, it is concluded that gas-phase branching and breaking need not be considered in the quenching of lean-to-stoichiometric propane-oxygen-nitrogen flames.

Evaluation of the effects of incomplete destruction of active particles at the walls (eq. (10) and fig. 1) shows that the efficiency of destruction ε cannot be very small. Comparison of figures 1 and 3 supports this conclusion; the simple theory, subject to the assumption $\varepsilon = 1$, correlates the quenching data much better than does equation (10).

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This discussion and the conclusions drawn are based on quenching data for propane-oxygen-nitrogen mixtures. It is believed that the conclusions are valid for other hydrocarbon fuels as well, inasmuch as propane contains both primary and secondary carbon-hydrogen bonds, and is therefore representative of unbranched alkanes in general. However, it should be emphasized that the conclusions are meaningful only in connection with the general concepts of flame quenching by diffusion of active particles and that no proof has been advanced for these concepts.

CONCLUSIONS

General equations for quenching distance have been derived, based on the active-particle diffusion concept of quenching. The equations include the effects of gas-phase chain branching and breaking and of incomplete destruction of active particles at the walls.

All the available types of propane-quenching data for long rectangular slots may be well correlated by the simple theory, in which gas-phase chain breaking and branching are not included and complete destruction of active particles at the walls is assumed. The data represent about a thirtyfold variation in quenching distance, and include the effects of initial temperature, pressure, proportion of oxygen in the oxidant atmosphere, and propane concentration; however, only lean-to-stoichiometric mixtures are treated.

Data on the effects of initial temperature on quenching distance, which have not previously been treated, agree qualitatively with predicted trends.

Application of the simple theory to the data indicates that the temperature dependence assigned to the diffusion coefficients for active particles has some effect on the degree of correlation. For purposes of the theory, a dependence greater than $D \propto T^{1.67}$ (D is diffusion coefficient; T is temperature) is favored; however, this should not be taken as evidence for the true temperature dependence.

From the agreement of the data with the simple equation that ignores the complicating features, it is concluded that chain branching and breaking may be neglected in the treatment of quenching data for propane-oxygen-nitrogen systems. It is also concluded that the assumption of complete destruction of active particles on collision with the walls is valid. It should be emphasized, however, that the conclusions are meaningful only in connection with the general concepts of flame quenching by diffusion, and that no proof has been advanced for these concepts.

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Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, December 20, 1954

APPENDIX - QUENCHING BY PLANE-PARALLEL PLATES OF INFINITE EXTENT

For the case in which total destruction of active particles does not occur at the walls and in which chain breaking and branching may occur in the volume, the diffusion equation describing quenching by plane-parallel plates of infinite extent is given by (ref. 13)

$$\nabla \cdot D_i \nabla c_i + (f_i - g_i)\, c_i + c_{o,i} = 0 \qquad (A1)$$

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where, for the i^{th} species of active particles,

$\nabla \cdot D_i \nabla c_i$ rate of disappearance of active particles (per unit volume) due to diffusion to walls

$c_{o,i}$ rate of creation of active particles (per unit volume) by straight-chain reactions

$0 < (f_i - g_i)c_i$ rate of creation of active particles (per unit volume) due to branched-chain reactions

$0 < (g_i - f_i)c_i$ rate of destruction of active particles (per unit volume) due to chain-breaking reactions

If it is assumed that average, constant values may be used for D_i, equation (A1) may be written, in rectangular coordinates,

$$D_i \left(\frac{d^2 c_i}{dx^2} + \frac{d^2 c_i}{dy^2} + \frac{d^2 c_i}{dz^2} \right) + (f_i - g_i)c_i + c_{o,i} = 0 \qquad (A2)$$

Application to the case of the volume contained between plane-parallel plates of infinite extent and of separation d simplifies equation (A2) to

$$D_i \left(\frac{d^2 c_i}{dx^2} \right) + (f_i - g_i)c_i + c_{o,i} = 0 \qquad (A3)$$

subject to the boundary conditions

$$\left.\begin{aligned} c_i &= c_{w,i} \\ x &= \pm d/2 \end{aligned}\right\}$$

and

$$\left.\begin{aligned} \frac{dc_i}{dx} &= 0 \\ x &= 0 \end{aligned}\right\} \qquad \text{(A4)}$$

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The three cases considered are

(1) Chain-branching reaction, $(f_i - g_i) > 0$

(2) Chain-breaking reaction, $(g_i - f_i) > 0$

(3) Straight-chain reaction, $(f_i - g_i) \equiv 0$

Over-all chain branching, $(f_i - g_i) > 0$. - Integration of equation (A3) gives (ref. 13)

$$c_i = A' \cos \sqrt{\frac{f_i - g_i}{D_i}}\, x + B' \sin \sqrt{\frac{f_i - g_i}{D_i}}\, x - \frac{c_{o,i}}{f_i - g_i} \qquad \text{(A5)}$$

Application of the boundary conditions (eq. (A4)) then yields

$$c_i = \left(\frac{c_{o,i}}{f_i - g_i} + c_{w,i}\right)\left(\frac{\cos \sqrt{\frac{f_i - g_i}{D_i}}\, x}{\cos \sqrt{\frac{f_i - g_i}{D_i}}\, \frac{d}{2}} - 1\right) + c_{w,i} \qquad \text{(A6)}$$

The active-particle chain length for a particular species is given by

$$\nu_i = \frac{\int_{-d/2}^{d/2} c_i\, dx}{c_{o,i}\tau_i d} = \left[\frac{1}{(f_i - g_i)\tau_i} + \frac{c_{w,i}}{c_{o,i}\tau_i}\right]\left(\frac{\tan \frac{d}{2}\sqrt{\frac{f_i - g_i}{D_i}}}{\frac{d}{2}\sqrt{\frac{f_i - g_i}{D_i}}} - 1\right) + \frac{c_{w,i}}{c_{o,i}\tau_i} \qquad \text{(A7)}$$

Equation (A7) remains finite as long as $\frac{d}{2}\sqrt{\frac{f_i - g_i}{D_i}} < \frac{\pi}{2}$. For this range of values, ν_i can be closely approximated by (ref. 13)

$$\nu_i = \left[\frac{1}{(f_i - g_i)\tau_i} + \frac{c_{w,i}}{c_{o,i}\tau_i}\right]\left[\frac{8d^2(f_i - g_i)}{\pi^4 D_i}\right]\left[\frac{1}{1 - \frac{d^2(f_i - g_i)}{\pi^2 D_i}}\right] + \frac{c_{w,i}}{c_{o,i}\tau_i} \tag{A8}$$

From reference 6

$$\sum_i \nu_i \frac{p_i}{p} = A = \sum_i \nu_i \frac{N_i}{N_t} \tag{A9}$$

Also

$$\tau_i = \frac{1}{(k_i N_f)} \tag{A10}$$

and

$$D_i = D_i^o \left(\frac{T_R}{T_O}\right)^n \left(\frac{1}{p}\right) \tag{A11}$$

Further,

$$c_{o,i} = k_i N_f N_i \left[1 + (f_i - g_i)\tau_i\right] \tag{A12}$$

and it is assumed that

$$\left.\begin{aligned} k_i &= k \\ f_i &= f \\ g_i &= g \end{aligned}\right\} \text{ for all i's}$$

and

$$c_{w,i} = (1 - \varepsilon)\ 0.7\ N_i \tag{A13}$$

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It should be noted that the form chosen for $c_{w,i}$ represents the simplest one that satisfies the criteria $c_{w,i} = 0$ for $\varepsilon = 1$ and $c_{w,i} = 0.7\ N_i$ for $\varepsilon = 0$.

Using equations (A8) to (A13) yields

$$d^2 = \frac{\left[A - \frac{(1 - \varepsilon)\ 0.7 \sum_i \frac{p_i}{p}}{kN_f + (f - g)}\right]\left(\frac{\pi^4}{8}\right)\left(\frac{T_R}{T_O}\right)^n}{kN_f \left[1 + \frac{(1 - \varepsilon)\ 0.7}{1 + \frac{kN_f}{f - g}}\right] \sum_i \frac{p_i}{D_i^o} \left[\frac{1}{1 - \frac{pd^2(f - g)}{\pi^2 D_i^o}\left(\frac{T_O}{T_R}\right)^n}\right]} \qquad (A14)$$

Over-all chain breaking, $(f_i - g_i) < 0$. - Integration of equation (A3) gives (ref. 13)

$$c_i = A'' \cosh \sqrt{\frac{g_i - f_i}{D_i}}\, x + B'' \sinh \sqrt{\frac{g_i - f_i}{D_i}}\, x + \frac{c_{o,i}}{g_i - f_i} \qquad (A15)$$

Application of the boundary conditions (eq. (A4)) then yields

$$c_i = \left(\frac{c_{o,i}}{g_i - f_i} - c_{w,i}\right)\left(1 - \frac{\cosh \sqrt{\frac{g_i - f_i}{D_i}}\, x}{\cosh \sqrt{\frac{g_i - f_i}{D_i}}\, \frac{d}{2}}\right) + c_{w,i} \qquad (A16)$$

The active-particle chain length for a given species is given by

$$\nu_i = \frac{\int_{-d/2}^{d/2} c_i\, dx}{c_{o,i} \tau_i d}$$

Thus,

$$\nu_i = \left[\frac{1}{(g_i - f_i)\tau_i} - \frac{c_{w,i}}{c_{o,i}\tau_i}\right]\left(1 - \frac{\tanh \frac{d}{2} \sqrt{\frac{g_i - f_i}{D_i}}}{\frac{d}{2} \sqrt{\frac{g_i - f_i}{D_i}}}\right) + \frac{c_{w,i}}{c_{o,i}\tau_i} \qquad (A17)$$

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For values of $(g_i - f_i)\, d^2/D_i < 1$, equation (A17) may be very closely approximated by

$$\nu_i = \left[\frac{1}{(g_i - f_i)\tau_i} - \frac{c_{w,i}}{c_{o,i}\tau_i}\right]\left[\frac{d^2(g_i - f_i)}{12\, D_i}\right]\left[1 - \frac{d^2(g_i - f_i)}{10\, D_i}\right] + \frac{c_{w,i}}{c_{o,i}\tau_i} \tag{A18}$$

If, on the other hand, $(g_i - f_i)\, d^2/D_i > 2$, equation (A17) can be very closely approximated by

$$\nu_i = \left[\frac{1}{(g_i - f_i)\tau_i} - \frac{c_{w,i}}{c_{o,i}\tau_i}\right]\left(1 - \frac{1}{\frac{d}{2}\sqrt{\frac{g_i - f_i}{D_i}}}\right) + \frac{c_{w,i}}{c_{o,i}\tau_i} \tag{A19}$$

First, for the case where $(g_i - f_i)\, d^2/D_i < 1$, equations (A9) to (A13) may be used, together with equation (A18), to show that

$$d^2 = \frac{12\left(\frac{T_R}{T_O}\right)^n \left[A - \frac{(1 - \varepsilon)\, 0.7 \sum_i \frac{p_i}{p}}{1 - \frac{g - f}{kN_f}}\right]}{kN_f\left[1 - \frac{(1 - \varepsilon)\, 0.7}{\frac{kN_f}{g - f} - 1}\right]\sum_i \frac{p_i}{D_i^o}\left[1 - \frac{p d^2 (g - f)}{10\, D_i^o}\left(\frac{T_O}{T_R}\right)^n\right]} \tag{A20}$$

Similarly, for the case where $(g_i - f_i)\, d^2/D_i > 2$, expression (A19) may be used to show that

$$d = \frac{\sum_i \left[\frac{kN_f}{g - f} - \frac{(1 - \varepsilon)\, 0.7}{1 - \frac{g - f}{kN_f}}\right] \frac{2p_i}{\sqrt{\frac{(g - f)\, p^3 \left(\frac{T_O}{T_R}\right)^n}{D_i^o}}}}{\sum_i \frac{p_i}{p}\left(\frac{kN_f}{g - f}\right) - A} \tag{A21}$$

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Straight-chain reaction, $(f_i - g_i) \equiv 0$. - In the case of a straight-chain reaction, equation (A3) reduces to

$$D_i \frac{d^2 c_i}{dx^2} + c_{o,i} = 0 \tag{A22}$$

Solution of equation (A22), subject to the boundary conditions (eq. (A4)), yields

$$c_i = \frac{c_{o,i}}{2 D_i} \left[\left(\frac{d}{2} \right)^2 - x^2 \right] \tag{A23}$$

The active-particle chain length for a given species is given by

$$\nu_i = \frac{\int_{-d/2}^{d/2} c_i dx}{c_{o,i} \tau_i d} = \frac{c_w}{c_{o,i} \tau_i} + \frac{d^2}{12 D_i \tau_i} \tag{A24}$$

Setting $c_{o,i} = k_i N_f N_i$ and using equations (A9) to (A11), (A13), and (A24), together with the assumption that $k_i = k$ for all i's, the following equation is obtained for the quenching distance:

$$d^2 = \frac{12 \left(\frac{T_R}{T_o} \right)^n \left[A - \frac{0.7 (1 - \varepsilon)}{p} \sum_i p_i(eq) \right]}{k N_f \sum_i \left(\frac{p_i}{D_i^o} \right)} \tag{A25}$$

It is interesting to note that the geometry effect, given in reference 6 for plane-parallel plates and for cylindrical tubes, remains unchanged as a result of the assumption of nonzero active-particle concentrations at the wall. This follows from the fact that solution of the diffusion equation for cylinders

$$\frac{1}{r} \frac{d}{dr} \left(r \frac{dc_i}{dr} \right) + \frac{c_{o,i}}{D_i} = 0 \tag{A26}$$

subject to the boundary conditions

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$$\left.\begin{aligned} c_i &= c_w \quad \text{at the walls} \\ (dc_i/dr) &= 0 \quad \text{at} \quad r = 0 \end{aligned}\right\} \tag{A27}$$

yields, for the chain length,

$$\nu_{c,i} = \frac{d_c^2}{32\, D_i \tau_i} + \frac{c_{w,i}}{c_{o,i} \tau_i} \tag{A28}$$

Thus, if $c_{w,i}$ is taken to be the same for both plane-parallel plates and cylindrical tubes, the geometry effect given in reference 6 remains unchanged.

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TABLE I. - CALCULATED PARTIAL PRESSURES OF ACTIVE PARTICLES AND EQUILIBRIUM ADIABATIC FLAME TEMPERATURES

Propane-air mixtures at 1 atm and various initial temperatures.

Propane in air, percent by volume	Initial temperature, °K	Partial pressure of H atom, atm	Partial pressure of O atom, atm	Partial pressure of OH radical, atm	Equilibrium flame temperature, °K
3.00	0	0.01×10^{-4}	0.16×10^{-4}	2.77×10^{-4}	1733
	300	.10	1.03	9.64	1941
	400	.22	1.76	13.49	2011
	600	.85	4.60	25.17	2148
	700	1.53	7.03	33.10	2214
3.25	0	0.04×10^{-4}	0.39×10^{-4}	5.33×10^{-4}	1843
	400	.65	3.06	20.52	2108
	600	2.00	6.89	34.63	2233
	700	3.27	9.85	43.53	2293
3.50	0	0.14×10^{-4}	0.77×10^{-4}	8.96×10^{-4}	1949
	300	.96	3.06	22.12	2134
	400	1.62	4.46	27.87	2193
	600	4.06	8.88	43.24	2304
	700	6.06	12.09	52.49	2357
4.03	0	1.50×10^{-4}	1.01×10^{-4}	13.19×10^{-4}	2122
	300	4.91	3.61	28.90	2273
	400	6.37	4.85	34.20	2313
	600	11.55	9.18	50.11	2401
	700	15.19	12.26	59.52	2444
4.50	0	2.80×10^{-4}	0.08×10^{-4}	3.66×10^{-4}	2073
	400	10.82	1.73	20.95	2312
	600	18.60	4.88	37.92	2414
	700	23.79	7.40	48.19	2462
5.00	0	2.14×10^{-4}	0.01×10^{-4}	0.91×10^{-4}	1966
	300	7.34	.12	4.83	2161
	400	10.51	.29	7.87	2229
	600	20.40	1.30	18.84	2358
	700	27.36	2.50	27.32	2419
6.00	0	0.68×10^{-4}	----	0.06×10^{-4}	1762
	300	3.18	----	.50	1958
	400	5.07	----	.93	2029
	600	12.26	0.05×10^{-4}	3.05	2175
	700	18.47	.14	5.26	2249

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TABLE II. - DIFFUSION COEFFICIENTS

FOR ACTIVE PARTICLES

Diffusion coefficients	$^{a}\psi_1$	$^{b}\psi_2$
D_H, cm^2/sec (300° K, 1 atm)	1.80	1.02
D_O, cm^2/sec (300° K, 1 atm)	.40	.29
D_{OH}, cm^2/sec (300° K, 1 atm)	.28	.26
n, $(D \propto T^n)$	2.00	1.67

[a]Ref. 16.
[b]Diffusion coefficients into unburned stoichiometric (4.03 percent by volume) propane-air mixture; ref. 7.

TABLE III. - OBSERVED AND PREDICTED VARIATION OF

QUENCHING DISTANCE WITH INITIAL TEMPERATURE

Propane in air, percent by volume	m (Observed,[a] $d \propto T_0^{-m}$)	m_1 (Predicted, $\psi_1^{1/2} \propto T_0^{-m_1}$)	m_2 (Predicted, $\psi_2^{1/2} \propto T_0^{-m_2}$)
3.00	0.90	0.54	1.06
3.25	.75	.49	1.00
3.50	.68	.38	.90
4.03	.60	.34	.85

[a]Data from ref. 9.

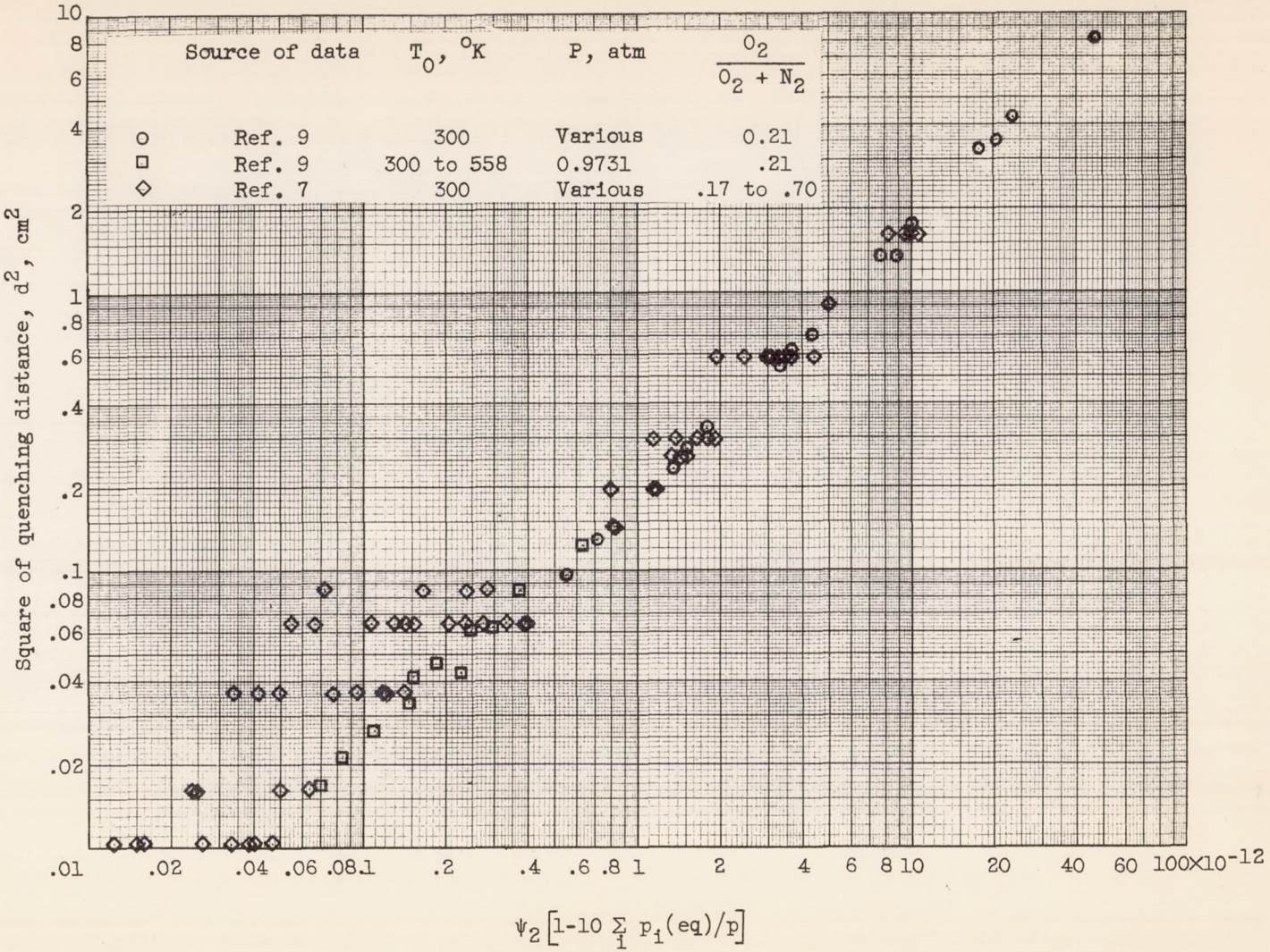
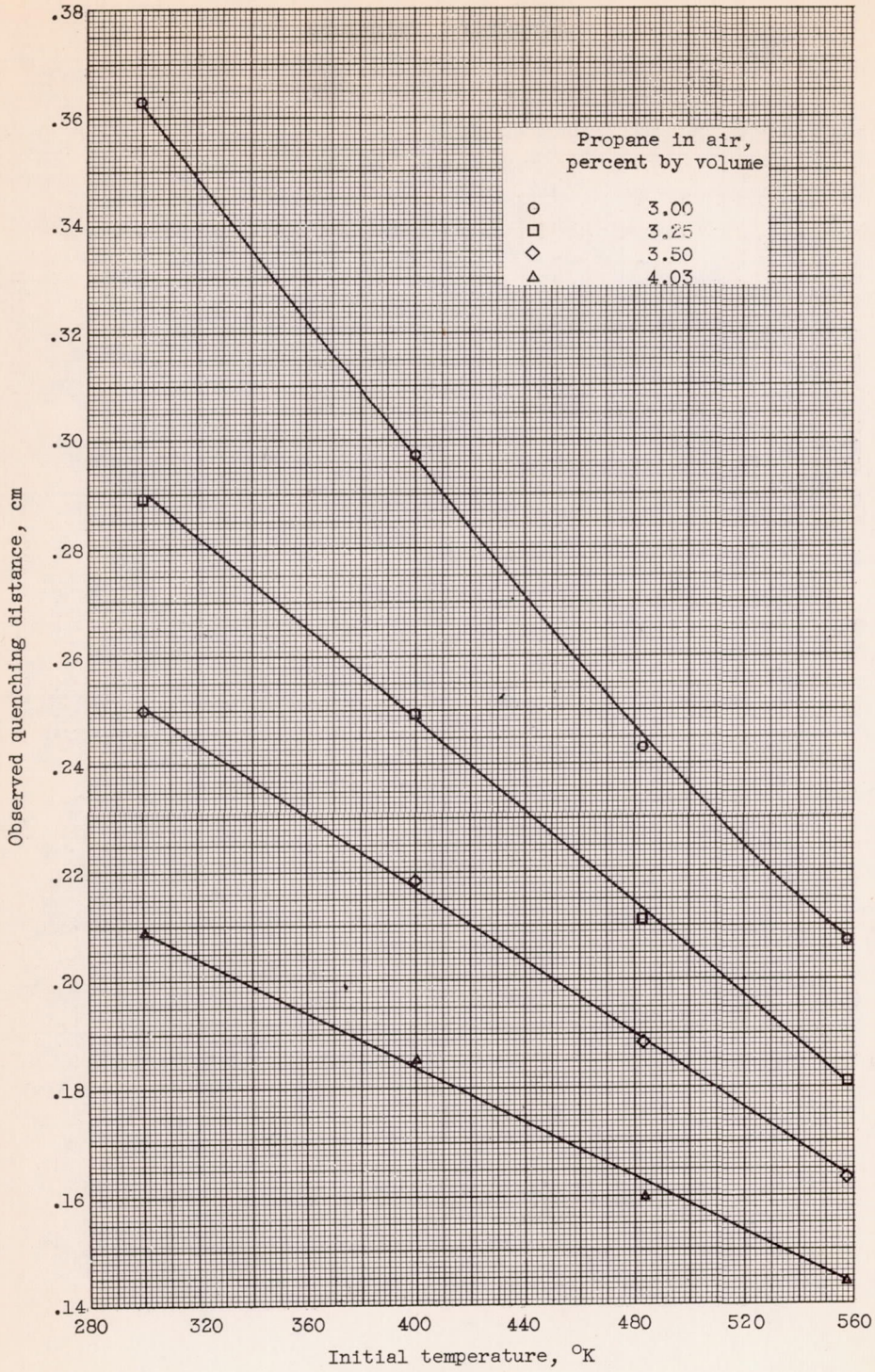
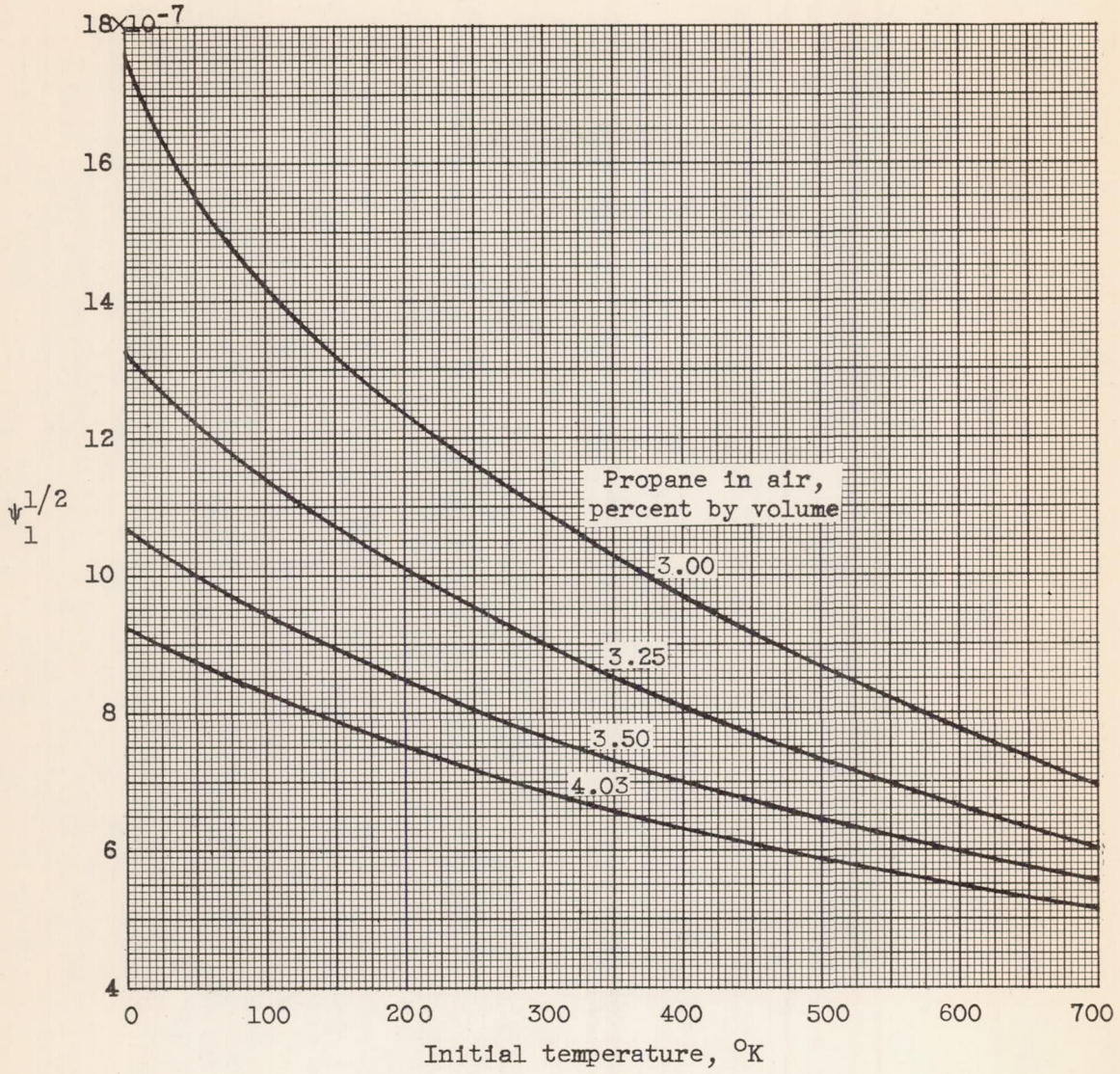


Figure 1. - Typical correlation of quenching-distance data with consideration of incomplete destruction of active particles at wall.



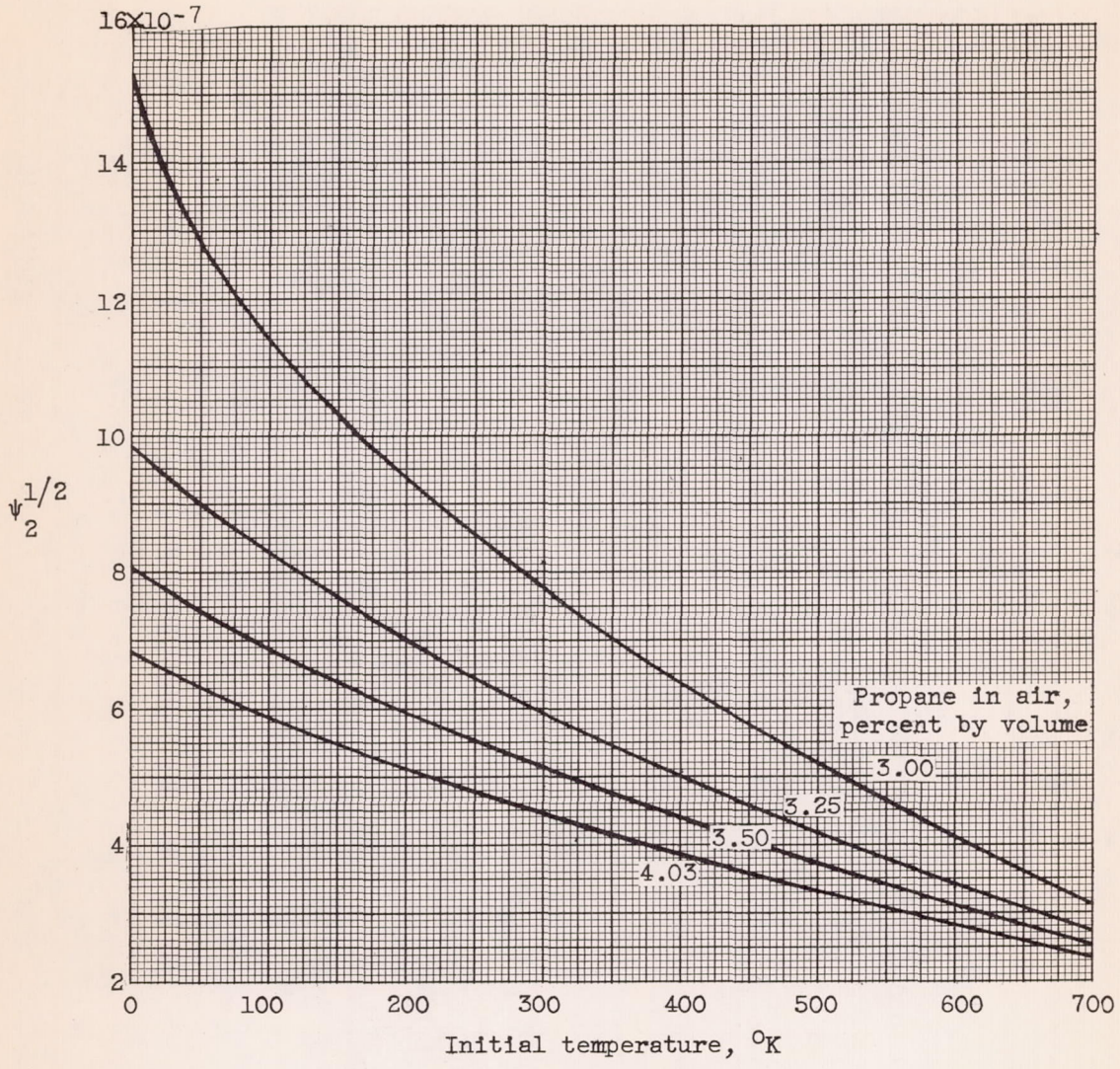
(a) Experimental; data from reference 9.

Figure 2. - Observed and predicted effects of initial temperature on quenching distance.



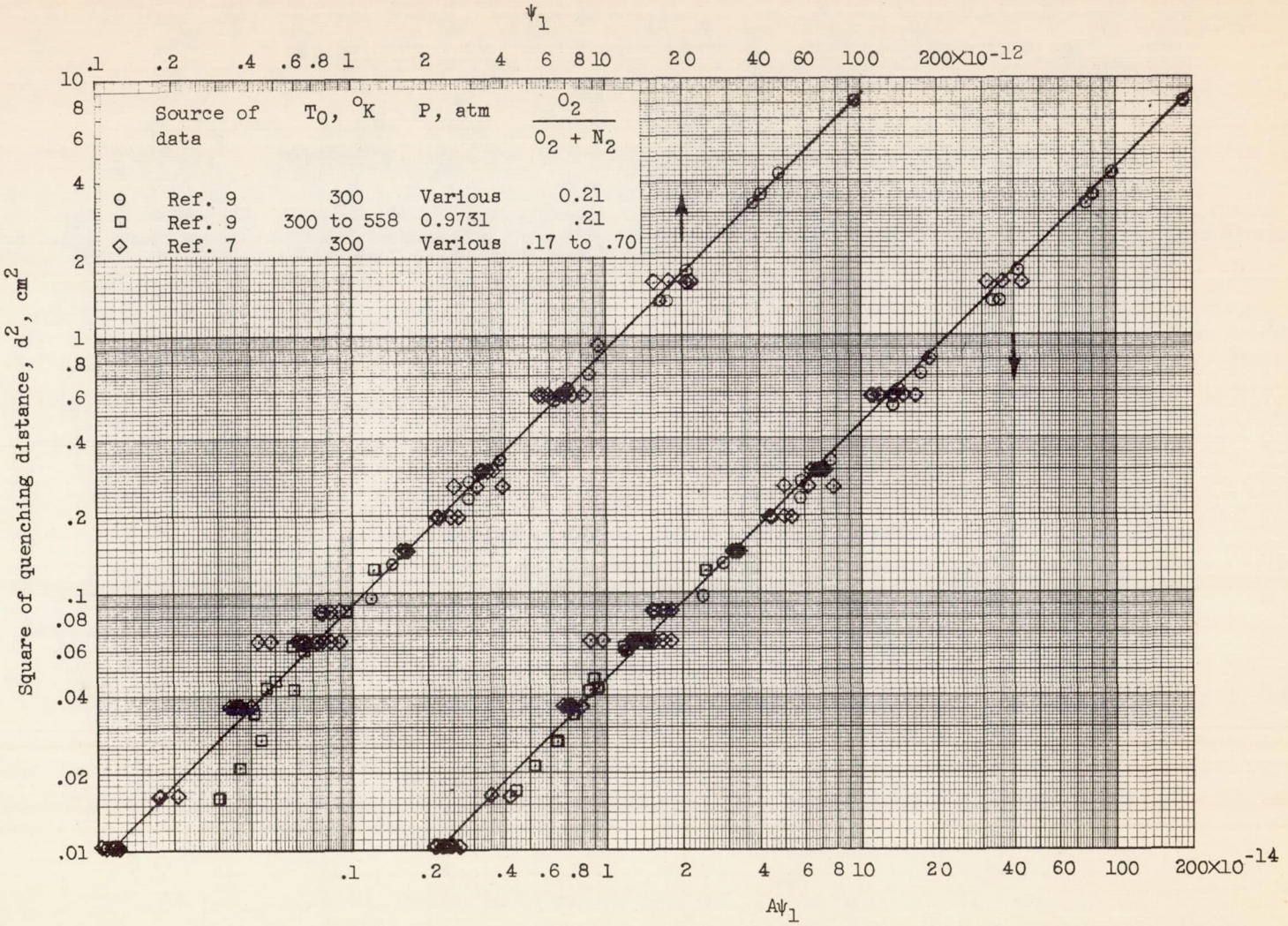
(b) Predicted; $D \propto T^2$.

Figure 2. - Continued. Observed and predicted effects of initial temperature on quenching distance.



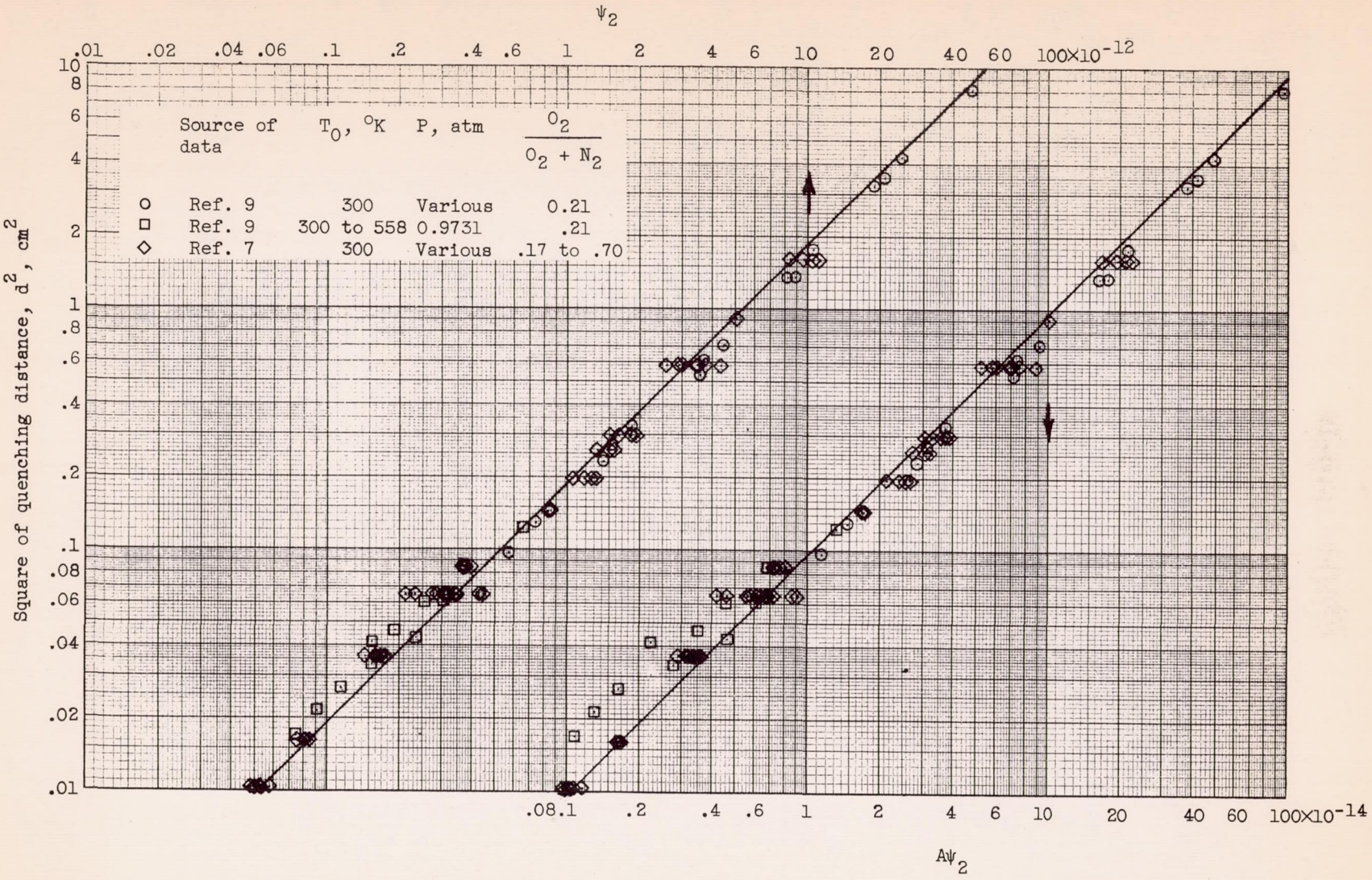
(c) Predicted; $D \propto T^{1.67}$.

Figure 2. - Concluded. Observed and predicted effects of initial temperature on quenching distance.



(a) $D \propto T^2$.

Figure 3. - Correlation of quenching-distance data by means of equation (9).



(b) $D \propto T^{1.67}$.

Figure 3. - Concluded. Correlation of quenching-distance data by means of equation (9).

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